

Vibrational Isotope Effect of Planar Molecules by the Low Rank Perturbation Method: Deuterated Ethylenes

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Planar molecules A and B, which are identical except for isotopic substitutions at various atomic sites τ , are considered. Out-of-plane frequencies ω_k and normal modes Ψ_k of the perturbed isotopic molecule B are expressed in terms of out-of-plane frequencies ν_i and out-of-plane normal modes Φ_i of unperturbed molecule A. Complete specification of unperturbed normal modes Φ_i is not required. All that is needed are amplitudes $\langle \tau | \Phi_i \rangle$ of normal modes Φ_i at sites τ of isotopic substitution. The interlacing rule that interlaces frequencies ω_k with frequencies ν_k is derived. The method is applied to all deuterated ethylenes. Out-of-plane frequencies of deuterated ethylenes are in excellent agreement with the interlacing rule. There is only one serious discrepancy, which might be due to an experimental error. In the ethylene case, out-of-plane amplitudes $\langle \tau | \Phi_i \rangle$ are determined by symmetry alone. Hence, out-of-plane frequencies and normal modes of all deuterated ethylenes depend only on the three experimental out-of-plane frequencies of ethylene. Standard error of the calculated out-of-plane frequencies (expressed in cm^{-1}) is only 2.92 cm^{-1} .

Key words: vibrational isotope effect, low rank perturbation, deuterated ethylenes, out-of-plane vibrations

INTRODUCTION

To study molecular vibrations, one can use the classical model of the molecule where the nuclei are represented by mathematical points with

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masses. Displacements of the nuclei from equilibrium positions can be described by Cartesian co-ordinates. If the molecule contains n nuclei, there are $3n$ such generic coordinates:

$$\xi_1, \xi_2, \dots, \xi_{3n}.$$

Potential energy V can be expressed as a function of these coordinates: $V = V(\xi_1, \xi_2, \dots, \xi_{3n})$. It is convenient to expand this expression in Taylor series. The first term of this expansion is a constant term, which can be equated to zero. The second term contains first derivatives of the potential energy V , and in the equilibrium position these derivatives must be zero. In the so called harmonic approximation, one neglects cubic and higher-order terms, retaining only quadratic terms.¹⁻³ In this approximation the potential energy is

$$V = \sum_{i < j} f_{ij} \xi_i \xi_j$$

where $f_{ij} = (\partial^2 V / \partial \xi_i \partial \xi_j)_0$ are force constants expressed in Cartesian coordinates.

Kinetic energy can be also expressed in terms of Cartesian displacements from equilibrium

$$T = \frac{1}{2} \sum_{i=1}^{3n} m_i \left(\frac{d\xi_i}{dt} \right)^2.$$

In order to obtain more compact expressions, one usually replaces coordinates ξ_i with mass-weighted coordinates $q_i = m_i^{1/2} \xi_i$.¹⁻³ However, since we are interested in the effects of isotope substitutions, it is more convenient to retain explicit dependence on atomic masses.^{4,5} The solution of the above system, consisting of n masses connected by harmonic forces, leads to the following generalized eigenvalue equation

$$\mathbf{F}|\Phi_i\rangle = \lambda_i \mathbf{M}|\Phi_i\rangle. \quad (1)$$

In this equation, \mathbf{F} and \mathbf{M} are $3n$ order hermitian matrices. Matrix \mathbf{F} is a force field matrix with matrix elements f_{ij} , while matrix \mathbf{M} is a diagonal matrix containing masses of the nuclei. The first three diagonal elements correspond to the mass of the first nucleus, next three to the mass of the second nucleus, *etc.* Eigenvectors $|\Phi_i\rangle$ represent normal vibrations, while the corresponding eigenvalues λ_i are related to vibrational frequencies ν_i by the relation

$$\lambda_i = 4\pi^2 \nu_i^2. \quad (1')$$

Due to translational and rotational symmetry, in the case of nonlinear molecules there are six nonproper vibrations $|\Phi_i\rangle$ with zero frequency $\nu_i = 0$. Three nonproper vibrations correspond to the translations in the direction of coordinate axes, while another three nonproper vibrations correspond to the rotations around coordinate axes. In the case of a linear molecule, there are only two rotations. We will assume that the molecule is rigid, and that there are no additional zero frequency vibrations.

Consider now molecule B, which is identical to the initial molecule A, except for the substitution of ρ atoms by isotope atoms. To a very good approximation this substitution will not affect the potential energy.¹⁻³ Hence, the force field matrix \mathbf{F} remains the same, and only matrix \mathbf{M} containing atomic masses will change. Thus, the perturbed isotope equation is

$$\mathbf{F}|\Psi_k\rangle = \varepsilon_k (\mathbf{M} + \Delta\mathbf{M})|\Psi_k\rangle. \quad (2)$$

where matrix $\Delta\mathbf{M}$ describes the change in the masses of isotopically substituted atoms.

Eigenvectors $|\Psi_k\rangle$ are perturbed vibrations, while the corresponding eigenvalues ε_k are related to perturbed frequencies ω_k by the relation

$$\varepsilon_k = 4\pi^2 \omega_k^2 \quad (2')$$

in analogy to (1').

Perturbed equation (2) can be efficiently treated by the Low Rank Perturbation (LRP) method.⁴ In the LRP approach, it is convenient to distinguish cardinal and singular eigenvalues of the perturbed equation. By definition, an eigenvalue ε_k of Eq. (2) is »cardinal« if it differs from all the unperturbed eigenvalues, *i.e.* if $\varepsilon_k \notin \{\lambda_i\}$. Otherwise, it is singular.⁴ In view of relations (1') and (2'), perturbed frequency ω_k is cardinal if it differs from all the unperturbed frequencies, *i.e.* if $\omega_k \notin \{\nu_i\}$. Otherwise, it is singular.

In general, we will interchangeably talk about »unperturbed eigenvalues λ_i «, and about »unperturbed frequencies ν_i «. Similarly, we will talk about »perturbed eigenvalues ε_k « or equivalently about »perturbed frequencies ω_k «. In view of relation (1'), one can easily replace unperturbed eigenvalues λ_i with unperturbed frequencies ν_i , and *vice versa*. Similarly, one can replace perturbed eigenvalues ε_k with perturbed frequencies ω_k , and *vice versa*.

OUT-OF-PLANE VIBRATIONS OF PLANAR MOLECULES

In the case of planar molecules, LRP relations substantially simplify.⁵ In-plane and out-of-plane vibrations are separate, and the treatment of

out-of-plane vibrations is particularly simple. If the molecule contains n atoms, there are n degrees of freedom perpendicular to molecular plane. Hence, there are n out-of-plane vibrations. Three out-of-plane vibrations are nonproper. One corresponds to the translation in the direction perpendicular to molecular plane, while the other two correspond to the rotations around two in-plane axes. Hence, there are $n - 3$ proper out-of-plane vibrations. Similarly, one finds that there are $2n - 3$ proper in-plane vibrations.

Let $|\Phi_i\rangle$ denote proper out-of-plane vibrations of this unperturbed molecule, and let ν_i be the corresponding frequencies. We label different atoms in a generic way with Greek letters α and β , and we label atoms that are exchanged by an isotope with Greek letters μ and τ . We assume that in a perturbed molecule there are ρ such atoms. Further, we denote a unit displacement in the out-of-plane direction at atom α as $\text{ket}|\alpha\rangle$. According to this notation, $\langle\alpha|\Phi_i\rangle$ is the amplitude of the out-of-plane vibration $|\Phi_i\rangle$ at atom α .

Matrices \mathbf{M} and $\Delta\mathbf{M}$ can be now written as

$$\mathbf{M} = \sum_{\alpha}^n |\alpha\rangle m_{\alpha} \langle\alpha| \quad \Delta\mathbf{M} = \sum_{\mu}^{\rho} |\mu\rangle \Delta m_{\mu} \langle\mu|$$

where m_{α} is the mass of atom α , while Δm_{μ} is the change of the mass of atom μ by isotope substitution.

Vibrations $|\Phi_i\rangle$ can be always orthonormalized according to

$$\langle\Phi_i|\mathbf{M}|\Phi_j\rangle = \delta_{i,j} \quad (3)$$

or explicitly $\sum_{\alpha}^n \langle\Phi_i|\alpha\rangle m_{\alpha} \langle\alpha|\Phi_j\rangle = \delta_{i,j}$. If the unit displacements $|\alpha\rangle$ are replaced by the mass-weighted unit displacements $|\alpha'\rangle = m_{\alpha}^{1/2}|\alpha\rangle$, relation (3) can be written in a more familiar form $\sum_{\alpha}^n \langle\Phi_i|\alpha'\rangle \langle\alpha'|\Phi_j\rangle = \delta_{i,j}$. However, since

we are interested in the isotopic effect, we will retain explicit dependence on masses in all formulas.

Nonproper vibrations $|\Phi_{Tz}\rangle$, $|\Phi_{Rx}\rangle$ and $|\Phi_{Ry}\rangle$, corresponding to the translation perpendicular to the molecular plane and to rotations around two in-plane axes are⁵

$$|\Phi_{Tz}\rangle = \frac{1}{\sqrt{M}} \sum_{\alpha}^n |\alpha\rangle \quad |\Phi_{Rx}\rangle = \frac{1}{\sqrt{I_x}} \sum_{\alpha}^n y_{\alpha} |\alpha\rangle \quad |\Phi_{Ry}\rangle = \frac{1}{\sqrt{I_y}} \sum_{\alpha}^n x_{\alpha} |\alpha\rangle. \quad (4)$$

In order for these nonproper vibrations to satisfy orthonormality relation (3), the origin of the coordinate system should be situated in the molecular center of mass, and coordinate axes should coincide with the principal axes.⁵ By convention, z -axis is perpendicular to the molecular plane,

while x - and y -axes are in the molecular plane. M is molecular mass, I_x and I_y are moments of inertia with respect to x - and y -axes, while x_α and y_α are x - and y -coordinates of the α -th atom.

Using the LRP method one can prove the following theorem:⁵

Theorem:

Let λ_i be the unperturbed out-of-plane eigenvalues. Let further the unperturbed out-of-plane vibrations be orthonormalized according to Eq. (3). Then:

a) $\varepsilon_k \notin \{\lambda_i\}$ is the perturbed out-of-plane eigenvalue if and only if it is a root of the equation

$$f(\varepsilon) \equiv \left| \Omega(\varepsilon) + \frac{\Delta \mathbf{M}^{-1}}{\varepsilon} \right| = 0 \quad (5)$$

where Ω is a $\rho \times \rho$ Hermitian matrix with matrix elements:

$$\Omega_{\mu\tau}(\varepsilon) = \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\mu x_\tau}{I_y} + \frac{y_\mu y_\tau}{I_x} \right] + \sum_i^{n-3} \frac{\langle \mu | \Phi_i \rangle \langle \Phi_i | \tau \rangle}{\varepsilon - \lambda_i}, \quad \mu, \tau = 1, \dots, \rho \quad (6a)$$

while $\Delta \mathbf{M}^{-1}$ is a $\rho \times \rho$ diagonal matrix with matrix elements

$$\Delta \mathbf{M}_{\mu\tau}^{-1} = \frac{\delta_{\mu\tau}}{\Delta m_\tau}. \quad (6b)$$

b) Let $\varepsilon_0 \notin \{\lambda_i\}$ be the perturbed out-of-plane eigenvalue. Each vibration Ψ corresponding to this eigenvalue is of the form

$$|\Psi\rangle = \frac{1}{\varepsilon_0} \left[T |\Phi_{Tz}\rangle + R_x |\Phi_{Rx}\rangle + R_y |\Phi_{Ry}\rangle \right] + \sum_i^{n-3} \frac{\langle \Phi_i | \tau \rangle C_\tau}{\varepsilon_0 - \lambda_i} |\Phi_i\rangle \quad (7a)$$

where quantities T , R_x and R_y are

$$T = \frac{1}{\sqrt{M}} \sum_\tau^\rho C_\tau, \quad R_x = \frac{1}{\sqrt{I_x}} \sum_\tau^\rho y_\tau C_\tau, \quad R_y = \frac{1}{\sqrt{I_y}} \sum_\tau^\rho x_\tau C_\tau, \quad (7b)$$

and where coefficients C_τ are components of a column vector \mathbf{C} , which is the (nontrivial) solution of the matrix equation

$$\left| \Omega(\varepsilon_0) + \frac{\Delta \mathbf{M}^{-1}}{\varepsilon_0} \right| \mathbf{C} = 0. \quad (8)$$

In addition, coefficients C_τ satisfy

$$C_\tau = -\varepsilon_0 \Delta m_\tau \langle \tau | \Psi \rangle, \quad \tau = 1, \dots, \rho. \quad (9)$$

Conversely, if ε_0 is the perturbed eigenvalue, each state Ψ of the form Eq. (7), where coefficients C_τ are the (nontrivial) solution of the linear set (8), is the corresponding vibration. Moreover, coefficients C_τ satisfy (9).

There are similar relations for in-plane vibrations. The proof of these relations will be given elsewhere.⁵

In the above relations, $|\Phi_i\rangle$ are unperturbed out-of-plane vibrations that are orthonormalized according to Eq. (3). Scalar product $\langle\mu|\Phi_i\rangle$ is a displacement of vibration $|\Phi_i\rangle$ at the isotope atom μ in the z -direction.

According to relations (7) and (8), each column vector \mathbf{C} which is a nontrivial solution of matrix equation (8) produces a normal mode (7) that corresponds to the perturbed eigenvalue ε_0 . If there are a few of such linearly independent vectors, eigenvalue ε_0 is degenerate. One can prove the following lemma:⁵

Lemma: Let $\varepsilon_0 \notin \{\lambda_i\}$ be the perturbed out-of-plane eigenvalue. The degeneracy of this eigenvalue equals the number of linearly independent solutions \mathbf{C} to relation (8).

In particular, each perturbed eigenvalue $\varepsilon_0 \notin \{\lambda_i\}$ is at most ρ -degenerate.

The above theorem gives a complete solution concerning the cardinal $\omega_k \notin \{\nu_i\}$ out-of-plane frequencies and the corresponding normal modes of the perturbed molecule. In order to apply this theorem, one has to know the unperturbed frequencies ν_i and unperturbed amplitudes $\langle\tau|\Phi_i\rangle$. However, not all amplitudes $\langle\alpha|\Phi_i\rangle$ are required. One has to know only amplitudes $\langle\tau|\Phi_i\rangle$ at the atoms that are substituted by an isotope. First, one solves equation (5), $f(\varepsilon)=0$. Each root ε_0 of this equation determines the perturbed frequency $\omega_0 = \sqrt{\varepsilon_0} / 2\pi$. Once a particular root ε_0 is found, one solves matrix equation (8) in order to obtain the (nontrivial) vector or vectors \mathbf{C} . This matrix equation is a set of ρ homogenous linear equations in ρ unknowns C_τ , and it is very easy to solve. Each nontrivial solution \mathbf{C} of this equation defines one normal mode according to relations (7).

The above theorem does not provide a solution for singular ($\omega_k \in \{\nu_i\}$) frequencies and vibrations. These singular solutions can be obtained in a similar way to cardinal solutions.^{4,5} For the sake of simplicity, we will not give these solutions here. In any case, singular solutions are much less important than cardinal solutions. Each singular perturbed frequency ω_k coincides with some unperturbed frequency ν_i , which makes it quite special. In most cases, a perturbed system contains only cardinal and no singular solutions.

By analogy with Eq. (3), perturbed normal modes (7a) can be orthonormalized according to

$$\langle \Psi_k | \mathbf{M} + \Delta \mathbf{M} | \Psi_l \rangle = \delta_{k,l}. \quad (3')$$

Due to the hermiticity of the eigenvalue equation (2), perturbed vibrations Ψ_k and Ψ_l corresponding to mutually distinct eigenvalues ε_k and ε_l are automatically orthogonal to each other according to Eq. (3'). However, perturbed vibrations (7a) are not properly normalized. If required, normalization can be easily performed. According to Eq. (7a), each perturbed vibration Ψ is a linear combination of unperturbed vibrations Φ_i : $\Psi = \sum_i c_i \Phi_i$. In order to normalize this vibration, one has to find

$$\langle \Psi | \mathbf{M} + \Delta \mathbf{M} | \Psi \rangle = \sum_i c_i^* c_i + \sum_{i,j} c_i^* c_j \langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle. \quad (10)$$

This requires evaluation of matrix elements $\langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle$. These matrix elements can be obtained using the expression for the perturbed matrix $\Delta \mathbf{M}$. One thus obtains

$$\langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle = \sum_{\mu}^{\rho} \langle \Phi_i | \mu \rangle \Delta m_{\mu} \langle \mu | \Phi_j \rangle. \quad (10')$$

It is important to note that by the LRP method one obtains perturbed frequencies and vibrations without any reference to force constants. Force constants are completely bypassed in this approach. This is highly convenient since different approaches lead to generally different sets of force constants. In addition, the LRP approach uses substantially less parameters than the direct application of relation (2) or its variant, *e.g.* the GF method, or alike. In order to find $n - 3$ out-of-plane perturbed frequencies and vibrations by the LRP method, one has to know $n - 3$ unperturbed frequencies $\nu_i = \sqrt{\lambda_i} / 2\pi$, $\rho(n - 3)$ unperturbed amplitudes $\langle \mu | \Phi_i \rangle$ at the positions of isotope substitution, 2ρ coordinates (x_{μ}, y_{μ}) of atoms that are substituted by an isotope, ρ isotope mass increments Δm_{μ} of these atoms, molecular mass M , and moments of inertia I_x and I_y . These essentially $(\rho + 1)n$ quantities are sufficient to determine all perturbed vibrations and frequencies. If the number of isotope substitutions is relatively small, this is substantially less than in general $O(n^2)$ force constants f_{ij} , which is usually required to solve equation (2) in a standard way. In addition, quantities related to atomic masses and to molecular geometry are usually much more reliable than force constants f_{ij} . Further, unperturbed frequencies can be treated as experimental quantities. Thus, it remains only to determine unperturbed amplitudes $\langle \mu | \Phi_i \rangle$. Only amplitudes $\langle \mu | \Phi_i \rangle$ of unperturbed vibrations at sites μ of isotopic substitution are required. No knowledge of amplitudes $\langle \alpha | \Phi_i \rangle$ at sites α , not affected by isotopic substitution, is needed. According to relations (10), this applies also to the normalization of perturbed vibrations.

In many cases, amplitudes $\langle \mu | \Phi_i \rangle$ are partly or completely determined by the molecular symmetry. Also, these amplitudes can be determined from

the out-of-plane frequencies of singly substituted molecules. Both approaches can be combined. We will demonstrate how this can be done by the example of deuterated ethylenes.

SINGLE ISOTOPE SUBSTITUTION

The above LRP method is particularly simple in the case of a single isotope substitution. Consider two planar molecules A and B_τ, which are identical except for one isotopic substitution at site τ. We consider A an unperturbed molecule and B_τ a perturbed molecule. Relations (5) and (6) now simplify to

$$f(\varepsilon) \equiv \sum_i^{n-3} \frac{\langle \tau | \Phi_i \rangle \langle \Phi_i | \tau \rangle}{\varepsilon - \lambda_i} + \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau} \right] = 0 \quad (11)$$

while relations (7) simplify to

$$|\Psi\rangle = \frac{1}{\varepsilon_0} \left[\frac{1}{\sqrt{M}} |\Phi_{Tz}\rangle + \frac{y_\tau}{\sqrt{I_x}} |\Phi_{Rx}\rangle + \frac{x_\tau}{\sqrt{I_y}} |\Phi_{Ry}\rangle \right] + \sum_i^{n-3} \frac{\langle \Phi_i | \tau \rangle}{\varepsilon_0 - \lambda_i} |\Phi_i\rangle \quad (12)$$

where ε_0 is a root of $f(\varepsilon)=0$. Each root ε_0 of $f(\varepsilon)$ determines an out-of-plane frequency $\omega_0 = \sqrt{\varepsilon_0} / 2\pi$ of the isotopic molecule B_τ. Once the root ε_0 of $f(\varepsilon)=0$ is found, the corresponding normal mode is given by Eq. (12). Thus, using relations (11) and (12), one finds all cardinal frequencies and vibrations of the perturbed molecule B_τ. According to Eq. (12), each root ε_0 of $f(\varepsilon)=0$ produces exactly one normal mode. Each cardinal frequency ($\omega_k \notin \{\nu_i\}$) is hence nondegenerate. Only singular frequencies (if any) may be degenerate.

In order to analyze the general distribution of cardinal and singular perturbed frequencies, it is convenient to distinguish active and passive unperturbed frequencies ν_i . Let frequency ν_i be η -degenerate and let $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$ be the corresponding unperturbed vibrations. Frequency ν_i is »passive« if the amplitudes of all these vibrations at the site of the isotope substitution are zero. Otherwise, this frequency is active.⁴ In other words, frequency ν_i is passive if $\langle \tau | \Phi_{is} \rangle = 0$ ($s=1, \dots, \eta$). Since atom τ at the isotope substitution position is not displaced during vibrations $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$, which correspond to passive frequency ν_i , it does not matter which atom is situated at this position. In other words, if frequency ν_i is passive, unperturbed vibrations $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$ are not affected by isotope substitution. Hence, the frequency $\omega_k = \nu_i$ is also a degenerate frequency of the perturbed system, and $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$ are the corresponding perturbed vibrations. Further, if ν_i is passive, function $f(\varepsilon)$ is not singular in the point $\varepsilon = \varepsilon_0 = 4\pi^2 \nu_i^2$. Hence, it may happen that $\varepsilon = \varepsilon_0$ is a root of $f(\varepsilon)=0$. If this is the case, than Ψ as given by relation (12) is yet another vibration that corresponds to frequency $\omega_k = \nu_i$.⁵

Thus, each root of $f(\varepsilon)=0$, not only the roots that satisfy $\varepsilon_0 \notin \{\lambda_i\}$, is a perturbed eigenvalue. On the other hand, if frequency ν_i is active and η -degenerate, one finds that, provided $\eta > 1$, $\omega_k = \nu_i$ is a $(\eta - 1)$ -degenerate perturbed frequency.⁵ Otherwise, $(\eta = 1)$, $\omega_k = \nu_i$ is not a perturbed frequency.

In conclusion, if ν_i is η -degenerate and passive, $\omega_k = \nu_i$ is either a η - or $(\eta+1)$ -degenerate frequency of the perturbed system. First η perturbed vibrations are the same as unperturbed vibrations $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$. An extra vibration exists if and only if $\varepsilon_0 = 4\pi^2\nu_i^2$ is a root of $f(\varepsilon)=0$. This extra vibration is of type (12). If however ν_i is η -degenerate and active and if $\eta > 1$, $\omega_k = \nu_i$ is a $(\eta-1)$ degenerate frequency of the perturbed system. These $(\eta-1)$ perturbed vibrations are linear combinations of unperturbed vibrations $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$.⁵

From equation (11), one can derive two important relations. The first is the interlacing relation, which interlaces perturbed and unperturbed frequencies. The second is the inversion relation that enables calculation of unperturbed amplitudes at the site of isotopic substitution from known unperturbed and perturbed frequencies.

In general, if in a mechanical system that exhibits harmonic oscillations one increases the mass of one or few particles without changing the potential energy, the frequencies of normal vibrations do not increase.^{1,3} These frequencies either decrease or remain the same. In particular, if frequencies ν_i of the initial molecule are arranged in the increasing order, and if frequencies ω_k of the heavier isotopic molecule are also arranged in the increasing order, then³

$$\omega_1 \leq \nu_1, \omega_2 \leq \nu_2, \dots, \omega_{3n} \leq \nu_{3n}. \quad (13)$$

The above order rule applies to all molecular frequencies. However, since in the case of a planar molecule in-plane and out-of-plane vibrations are separate, this rule applies separately to in-plane and separately to out-of-plane frequencies.

We will now derive the so called interlacing rule. This rule applies to out-of-plane vibrations of planar isotopic molecules A and B _{τ} , where molecule B _{τ} is identical to molecule A, except for a single isotope substitution at site τ . The interlacing rule implies the order rule, but it imposes a much stronger restriction to the range of possible values of frequencies ν_i and ω_k .

Assume that $\Delta m_\tau > 0$. Since $\langle \tau | \Phi_i \rangle \langle \Phi_i | \tau \rangle \geq 0$ function $f(\varepsilon)$ has a negative derivative for each $\varepsilon \notin \{\lambda_i\}$. In the point $\varepsilon = \lambda_i$ this function is singular unless the unperturbed eigenvalue λ_i is passive. This function is also singular in the point $\varepsilon = 0$. There is hence exactly one root of $f(\varepsilon)$ in each interval (λ_i, λ_j) where $\lambda_i < \lambda_j$ are two consecutive active eigenvalues. This applies also to in-

terval $(0, \lambda_s)$ where λ_s is the smallest active eigenvalue. Hence, if all unperturbed proper eigenvalues λ_i are nondegenerate and active, one finds

$$0 < \varepsilon_1 < \lambda_1 < \varepsilon_2 < \lambda_2 < \dots < \varepsilon_{n-3} < \lambda_{n-3}.$$

Thus, the $(n-3)$ eigenvalues ε_i of the perturbed equation are interlaced with the $(n-3)$ eigenvalues λ_i of the unperturbed equation. Due to relations (1') and (2'), the same is true of the corresponding frequencies.

The above interlacing relation is valid provided all unperturbed frequencies are active and mutually distinct. Using the properties of singular and passive frequencies, this condition can be relaxed. One thus obtains⁵

Interlacing rule:

Consider two n -atom planar molecules A and B, which differ by a single isotope substitution. Let molecule B be heavier than molecule A, and let ν_i and ω_k be proper out-of-plane frequencies of molecules A and B, respectively. Arrange these frequencies in the nondecreasing order. Then, these frequencies are interlaced according to

$$0 \leq \omega_1 \leq \nu_1 \leq \omega_2 \leq \nu_2 \leq \dots \leq \omega_{n-3} \leq \nu_{n-3}. \quad (14)$$

One easily finds the condition for a strict inequality to apply. If the two successive unperturbed frequencies are degenerate, one has $\nu_i = \omega_{i+1} = \nu_{i+1}$. If the two successive unperturbed frequencies ν_i and ν_{i+1} are distinct and active, one has strict inequality $\nu_i < \omega_{i+1} < \nu_{i+1}$, etc.

Interlacing relation (14) implies the order rule (13). However, the interlacing relation is more powerful. If ω_k is the k -th perturbed frequency, the order rule restricts this frequency only from one side ($\omega_k \leq \nu_k$), while the interlacing rule restricts it from both sides ($\nu_{k-1} \leq \omega_k \leq \nu_k$). Thus, the interlacing rule quite substantially restricts the range of possible values for perturbed and nonperturbed frequencies, and hence it can be used to facilitate frequency assignment. Also, the rule can be applied to the pair of isotopic molecules that differ in more than one isotope. For example, if A and B are two planar isotopic molecules that differ by two isotopic substitutions, one can consider the transition from molecule A to molecule B in two steps: from molecule A to intermediate molecule C, and from molecule C to molecule B. In each step only a single isotopic substitution is performed. Assume, for example, that both isotopes are heavier in molecule B. In that case, molecule C is heavier than molecule A, and molecule B is heavier than molecule C. Hence, if ν_i ' are nondecreasing out-of-plane frequencies of molecule C, the interlacing rule implies $\nu_{k-1} \leq \nu_k' \leq \nu_k$ (transition from A to C) and $\nu_{k-1}' \leq \omega_k \leq \nu_k'$ (transition from C to B). Combining these two results, one

finds the interlacing condition $\nu_{k-2} \leq \omega_k \leq \nu_k$. Similarly, if one of these two isotopes is heavier in molecule A, while another is heavier in molecule B, one finds the interlacing condition $\nu_{k-1} \leq \omega_k \leq \nu_{k+1}$, *etc.* In this way, one can generalize the interlacing rule to all multiple isotopic substitutions. Each such multiple isotopic substitution can be considered as a sequence of single isotopic substitutions. The introduction of each new isotope can shift (ordered) perturbed frequencies ω_k relative to (ordered) unperturbed frequencies ν_i only by one place. The direction in which this shift is performed (lowering or increasing these frequencies) depends on whether the isotope mass change is positive or negative.

We now turn to yet another consequence of the relation (11). This is the inversion relation by which one can deduce the unperturbed amplitudes $\langle \tau | \Phi_i \rangle$ from unperturbed and perturbed out-of-plane frequencies ν_i and ω_k .

Assume first that all unperturbed out-of-plane eigenvalues λ_i are nondegenerate and active. According to the interlacing rule, all perturbed eigenvalues ε_k are in this case cardinal. In particular, there are exactly $(n - 3)$ mutually distinct unperturbed eigenvalues λ_i , and also exactly $(n - 3)$ mutually distinct perturbed eigenvalues ε_k . In addition, all perturbed eigenvalues differ from all the unperturbed eigenvalues λ_i .

We now define matrix **A** and column vectors **C** and **X**

$$A_{k,i} = \frac{1}{\varepsilon_k - \lambda_i} \quad X_k = -\frac{1}{\varepsilon_k} \left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau} \right] \quad C_i = \langle \tau | \Phi_i \rangle \langle \Phi_i | \tau \rangle. \quad (15)$$

Matrix **A** is a square matrix of order $(n - 3)$, and vectors **C** and **X** are column vectors with $(n - 3)$ components each. Since each eigenvalue ε_k satisfies relation (11), matrix **A** and vectors **X** and **C** satisfy **AC** = **X**, and hence

$$\mathbf{C} = \mathbf{A}^{-1} \cdot \mathbf{X} \quad (16)$$

This is an inversion relation. Using this relation and the given out-of-plane unperturbed frequencies ν_i and out-of-plane isotope frequencies ω_k , one obtains squares of the unperturbed out-of-plane amplitudes at the isotope site.

Inversion relation (16) is derived under the assumption that all unperturbed frequencies are nondegenerate and active. These conditions can be relaxed. For example, if the unperturbed frequency ν_i is η -degenerate and if $\Phi_{i1}, \Phi_{i2}, \dots, \Phi_{i\eta}$ are the corresponding normal modes, one has to replace the coefficient C_i in relation (15) with the more general expression

$$C_i = \sum_{\kappa}^{\eta} \langle \tau | \Phi_{i\kappa} \rangle \langle \Phi_{i\kappa} | \tau \rangle. \quad (15a)$$

If there are $r < (n - 3)$ mutually distinct eigenvalues λ_i , there are also r mutually distinct cardinal eigenvalues ε_k , which are all roots of $f(\varepsilon)$. Matrix **A** is hence a square matrix of order $r < (n - 3)$, and relation (16) again applies. Finally, if a particular frequency ν_i is passive, one has $C_i = 0$, and this frequency should be omitted from the construction of matrix **A**.

In conclusion, in choosing the set $\{\lambda_i\}$ of unperturbed eigenvalues λ_i and the set $\{\varepsilon_k\}$ of perturbed eigenvalues ε_k , which are required for the construction of matrix **A** and vector **X**, the following rule applies: The set $\{\lambda_i\}$ should contain all mutually distinct active unperturbed out-of-plane eigenvalues. The set $\{\varepsilon_k\}$ should contain all mutually distinct perturbed eigenvalues that, in addition, differ from all the unperturbed eigenvalues $\lambda_i \in \{\lambda_i\}$. According to the above analysis, both sets contain the same number of elements, and **A** is a square matrix. The inversion relation now produces coefficients C_i (relation (15a)). Each coefficient C_i is a squared amplitude (or sum of such squared amplitudes) of the unperturbed normal mode (or modes) at the site of isotope substitution.

The inversion relation suggests a systematic method for obtaining out-of-plane frequencies and normal modes of all isotopomers of a given planar molecules. All one needs are experimental out-of-plane frequencies ν_i of unperturbed molecule, and various sets $\{\omega_k\}$ of out-of-plane frequencies of monosubstituted molecules.

Consider a planar molecule **A** and a set of monosubstituted planar molecules **B_τ**. Each molecule **B_τ** is identical to molecule **A**, except for a single isotopic substitution at site τ . Let $\{\nu_i\}$ be the set of all mutually distinct and (relative to the substitution site τ) active out-of-plane frequencies of molecule **A**. Let further $\{\omega_k\}_\tau$ be the set of all mutually distinct out-of-plane frequencies of molecule **B_τ** such that each $\omega_k \in \{\omega_k\}_\tau$ differs from all unperturbed frequencies $\nu_i \in \{\nu_i\}$. Each set $\{\omega_k\}_\tau$ contains the same number of elements as the corresponding unperturbed set $\{\nu_i\}$. Using relation (16) where matrix **A** and vector **X** are defined in terms of frequencies $\{\nu_i\}$ and $\{\omega_k\}_\tau$, one obtains vector **C**, which determines amplitude squares $\langle \tau | \Phi_i \rangle^2$ (or in case of degeneracy, the sum of such amplitudes) of unperturbed out-of-plane normal modes at the substitution site τ . In this way, by using only experimental frequencies of monosubstituted molecules **B_τ**, one can obtain amplitude squares of out-of-plane vibrations at all molecular sites of interest. According to relations (5)–(8), in order to obtain out-of-plane frequencies and normal modes of a polysubstituted molecule with isotopic substitutions at sites μ and τ , one has to know a relative sign of amplitudes $\langle \tau | \Phi_i \rangle$ and $\langle \mu | \Phi_i \rangle$ at these sites, in addition to absolute values of these amplitudes. In many cases, these relative signs are determined by the symmetry. Also, orthonormality relation (3) substantially restricts possible variations in these relative signs. Finally, one

can use a simple model, which need not be very sophisticated. This model should be good enough to obtain the relative signs of amplitudes $\langle \tau | \Phi_i \rangle$ and $\langle \mu | \Phi_i \rangle$ at different sites, but not necessarily good enough to obtain their absolute values. After this is done, one can obtain all out-of-plane frequencies and vibrations for any isotopomer. Thus, monosubstituted frequencies, in conjunction with molecular geometry and atomic masses, completely determine all polysubstituted frequencies and vibrations.

For example, there are nine out-of-plane normal modes in the case of benzene molecule. Due to symmetry all hydrogen positions are equivalent, and there is only one type of monodeuterated benzene. Hence, set of only 18 frequencies, nine benzene out-of-plane frequencies and nine monodeuterated benzene out-of-plane frequencies, is sufficient to obtain out-of-plane frequencies and normal modes for all bideuterated, trideuterated, etc. benzene molecules. In fact, due to the high symmetry of benzene molecule, even that much information is not needed, and it suffices to know only three out of nine monodeuterated frequencies.⁵

OUT-OF-PLANE VIBRATIONS OF DEUTERATED ETHYLENES

As an example, we apply the LRP approach to ethylene and deuterated ethylenes. Ethylene molecule is shown in Figure 1a. This molecule has three out-of-plane vibrations. We use frequency labels $\nu_4(A_{1u})$, $\nu_7(B_{1u})$ and $\nu_8(B_{2g})$, as this is done in Ref. 3. The corresponding out-of-plane normal modes are shown in Figure 1b), c) and d).

We first verify how well the experimental frequencies satisfy the interlacing rule. This is done in Table I. Experimental frequencies were

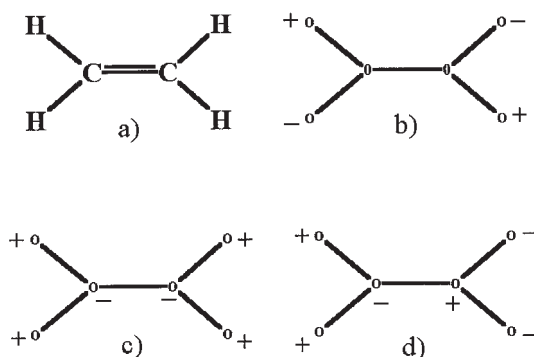


Figure 1. Ethylene molecule and ethylene out-of-plane vibrations. a) Ethylene molecule b) $\nu_4(A_{1u}) = 1024 \text{ cm}^{-1}$, vibration type $\chi_{\text{CH}_2}^{\text{CH}_2}$ c) $\nu_7(B_{1u}) = 949.3 \text{ cm}^{-1}$, vibration type ρ_{CH_2} d) $\nu_8(B_{2g}) = 943 \text{ cm}^{-1}$, vibration type ρ_{CH_2} .

TABLE I

Demonstration of the interlacing rule. Isotopic molecule B is identical to the isotopic molecule A, except for one hydrogen atom in molecule A which is replaced by deuterium in molecule B. Out-of-plane frequencies (in cm^{-1}) are taken from ref. [3]. All frequencies satisfy the interlacing rule, except for the two cases denoted with a question mark.

A	B	B		A		B		A		B		A
<i>d0</i>	<i>d1</i>	807 810	<	943	?	943 945	<	949.3	<	1001 1008	<	1024
<i>d1</i>	<i>ad2</i>	751 752	<	807 810	<	892	<	943 945	? ??	943	<	1001 1008
<i>d1</i>	<i>cisd2</i>	763	<	807 810	<	842	<	943 945	<	978	<	1001 1008
<i>d1</i>	<i>transd2</i>	725	<	807	<	863	<	943	<	987	<	1001 1008
<i>ad2</i>	<i>d3</i>	724	<	751 752	<	765	<	892	<	919	<	943
<i>cisd2</i>	<i>d3</i>	724	<	763	<	765	<	842	<	919	<	978
<i>transd2</i>	<i>d3</i>	724	<	725	<	765	<	863	<	919	<	987
<i>d3</i>	<i>d4</i>	720	<	724	<	729	<	765	<	780	<	919

taken from Ref. 3. In some cases, two distinct experimental frequencies were reported. A and B form a pair of isotopic molecules that differ in only one isotopic substitution. Molecule B has been chosen to be heavier than molecule A. For example, ethylene (*d0*) and monodeuterated ethylene (*d1*) form such a pair. Hence, the corresponding out-of-plane frequencies should satisfy the interlacing relation. Moreover, all out-of-plane ethylene frequencies are nondegenerate and active. Thus a strict inequality should apply everywhere in the interlacing relation (14).

Experimental frequencies are in very good agreement with the interlacing rule. There are only two exceptions. The first exception is a pair of frequencies $\nu_A = 943 \text{ cm}^{-1}$ and $\nu_B = 943 \text{ cm}^{-1}$ in comparison of ethylene (*d0*) and monodeuterated ethylene (*d1*) frequencies. According to the interlacing rule a strict inequality should apply in this case. Since an infinitesimal change in either experimental frequency can restore the validity of the interlacing rule, this is a very mild violation of the rule. Moreover, another reported experimental frequency — $\nu_B = 945 \text{ cm}^{-1}$ is in accord with this rule.

Another exception is the pair of frequencies $\nu_A = 945 \text{ cm}^{-1}$ and $\nu_B = 943 \text{ cm}^{-1}$ in comparison to monodeuterated (d1) and α -bideuterated (αd_2) ethylenes. Here interlacing rule predicts $\nu_A < \nu_B$, and data $\nu_A = 945 \text{ cm}^{-1}$ and $\nu_B = 943 \text{ cm}^{-1}$ are in clear violation of this prediction. However, another experimental frequency $\nu_A = 943 \text{ cm}^{-1}$ fits the interlacing rule much better. It should be noted that the frequency $\nu_A = 945 \text{ cm}^{-1}$ is obtained in a liquid phase, while the frequency $\nu_A = 943 \text{ cm}^{-1}$ is obtained in a gas phase. In general, frequencies obtained in a gas are more reliable. Looking at this violation of the interlacing rule from another point of view, one can say that this rule dismisses the frequency $\nu_A = 945 \text{ cm}^{-1}$ as incorrect.

In general, if the interlacing rule predicts strict inequality in a particular case, while experimental data produce equality, this is not a serious violation of this rule. In such cases, an infinitesimal change in the experimental values can restore the validity of the interlacing rule. More serious is the case when experimental data produce strict inequality which violates the interlacing rule. In this case, it is likely that experimental data are either wrong, or that the assignment of frequencies is wrong. Of course, the interlacing rule may also be wrong, since this rule strictly applies only in harmonic approximation. The effects of anharmonicity may violate this rule. Nevertheless, the fact that experimental data violate the interlacing rule is a sign for caution and for a detailed analysis of the frequencies in question.

Let us now consider the LRP derivation of deuterated frequencies and normal modes. In the LRP calculation following ethylene parameters were used:³

$$r_{CH} = 1.086 \text{ \AA}, \quad r_{CC} = 1.338 \text{ \AA}, \quad \alpha(\text{HCH}) = 117^\circ 30'.$$

In conjunction with atomic masses as expressed in atomic units $m_H = 1.0087$, $m_D = 2.0140$ and $m_C = 12.011$, these parameters determine the molecular mass, molecular geometry and moments of inertia. In particular, relations (4) give the amplitudes of the three nonproper vibrations at the substitution site.

Ethylene out-of-plane modes are shown in Figure 1. Their symmetry types, as well as the corresponding frequencies, are given in Table II.

All three ethylene out-of-plane normal modes are determined by the ethylene geometry and atomic masses of C and H atoms. Hence, there is no need to obtain amplitudes $\langle \tau | \Phi_i \rangle$ via inversion relation (16). From symmetry alone, one obtains amplitudes $\langle \tau | \Phi_i \rangle$ at the hydrogen atom: $\langle \tau | \Phi_4 \rangle = 0.4981$, $\langle \tau | \Phi_7 \rangle = 0.4609$ and $\langle \tau | \Phi_8 \rangle = 0.3976$. In addition, one obtains amplitudes at the carbon atom: $\langle C_\tau | \Phi_4 \rangle = 0.0000$, $\langle C_\tau | \Phi_7 \rangle = 0.0773$ and $\langle C_\tau | \Phi_8 \rangle = 0.1229$. These carbon amplitudes are not needed in the calculation of deuterium iso-

TABLE II

Experimental out-of-plane frequencies (in cm^{-1}) for the ethylene molecule. Data and frequency enumeration (ν_4 , ν_7 and ν_8) are from Ref. 3.

	Symmetry	Vibration type	ν (cm^{-1})
4	A_{1u}	$\chi_{\text{CH}_2}^{\text{CH}_2}$	(1024) (inactive)
7	B_{1u}	ρ_{CH_2}	949.3 (IR, gas)
8	B_{2g}	ρ_{CH_2}	943 (Raman, liquid)

tope effects, but they are required for the calculation of carbon isotope effects. Using the three unperturbed hydrogen amplitudes and experimental unperturbed frequencies, one can obtain perturbed out-of-plane frequencies and vibrations for all deuterated ethylenes. In applying relations (5) and (6), one has to observe the relative sign of amplitudes $\langle \tau | \Phi_i \rangle$ on different deuterated sites. These relative signs are determined by symmetry alone and they are obvious from Figure 1. Tables III and IV give deuterated frequencies that were calculated in this way. The agreement between theoretical (LRP) and experimental frequencies is very good. In the case of monodeuterated ethylene, there are two experimental values for each out-of-plane frequency, one obtained in a liquid phase and another in a gas phase. The largest error is in frequency $\nu_4 = 1008 \text{ cm}^{-1}$ which was obtained in a liquid phase. If in the case of monodeuterated ethylene one takes into account gas frequencies as more reliable, one obtains a standard error for all calculated frequencies in Tables III and IV to be only $\Delta = 2.92 \text{ cm}^{-1}$.

TABLE III

Comparison of theoretical (LRP) and experimental³ out-of-plane frequencies (cm^{-1}) for deuterated ethylenes $\text{C}_2\text{H}_3\text{D}$, *cis*- $\text{C}_2\text{H}_2\text{D}_2$ and *trans*- $\text{C}_2\text{H}_2\text{D}_2$. LRP frequencies were calculated using experimental ethylene frequencies from Ref. 3 (Table II). *) liquid.

		$\text{C}_2\text{H}_3\text{D}$			<i>cis</i> - $\text{C}_2\text{H}_2\text{D}_2$			<i>trans</i> - $\text{C}_2\text{H}_2\text{D}_2$		
Vibr.	Type	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.
4	χ	1001	999.4	-1.6	978	980.2	2.1	987	987.7	0.7
		1008*		-8.6						
7	ρ	943	945.7	2.7	842	841.7	-0.3	725	720.7	-4.3
		945*		0.7						
8	ρ	807	804.8	-2.1	763	757.4	-5.6	863*	864.7	1.7
		810*		-5.2						

TABLE IV

Comparison of theoretical (LRP) and experimental³ out-of-plane frequencies (cm^{-1}) for deuterated ethylenes $\alpha\text{-C}_2\text{H}_2\text{D}_2$, C_2HD_3 and C_2D_4 . LRP frequencies were calculated using experimental ethylene frequencies from Ref. 3 (Table II).

Vibr. Type	$\alpha\text{-C}_2\text{H}_2\text{D}_2$			C_2HD_3			C_2D_4		
	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.
4 χ	892	886.9	-5.1	724	720.6	-3.4	(729)	724.4	-4.6
7 ρ	751	749.5	-1.5	765	762.2	-2.8	720	718.1	-1.9
		752	-2.5						
8 ρ	943	945.7	2.7	919	918.9	0.1	780	778.6	-1.4

In conclusion, one can say that the calculated frequencies are in excellent agreement with experimental frequencies. The agreement between calculated and experimental frequencies seems to be better than expected from harmonic approximation. Thus, it is likely that unharmonicity effects partially cancel in the LRP approach.

The above LRP method can be used in yet another way. Experimental deuterated ethylene frequencies can be used in order to improve ethylene out-of-plane frequencies. In particular, ethylene out-of-plane frequency $\nu_4 = 1024 \text{ cm}^{-1}$ is relatively unreliable. This vibration is of symmetry type A_{1u} and it is inactive both in Raman and in IR. Hence one has to obtain this frequency indirectly, which makes it very prone to errors. One can consider ethylene out-of-plane frequencies as adjustable parameters, and try to adjust these frequencies in such a way as to minimize the standard error of calculated deuterated frequencies. If this is done, one obtains $\nu_4 = 1028.2 \text{ cm}^{-1}$, $\nu_7 = 950.1 \text{ cm}^{-1}$ and $\nu_8 = 942.2 \text{ cm}^{-1}$ as optimal ethylene out-of-plane frequencies. If the LRP calculation is done with these optimal ethylene frequencies, standard error for calculated deuterated frequencies decreases from $\Delta = 2.92 \text{ cm}^{-1}$ to $\Delta = 2.35 \text{ cm}^{-1}$. These optimal ethylene frequencies minimizing standard error differ from experimental values given in Table II by $\Delta\nu_4 = 4.2 \text{ cm}^{-1}$, $\Delta\nu_7 = 0.8 \text{ cm}^{-1}$ and $\Delta\nu_8 = -0.8 \text{ cm}^{-1}$. There is a negligible change of frequencies ν_7 and ν_8 . This is in accord with the fact that these frequencies are experimentally quite reliable. However, frequency ν_4 which is inactive changes much more. This indicates that ethylene frequency ν_4 is probably underestimated, and that the true value of this frequency should be closer to $\nu_4 = 1028 \text{ cm}^{-1}$ than to the reported value of $\nu_4 = 1024 \text{ cm}^{-1}$.

Once a particular perturbed frequency is obtained, one finds the corresponding normal modes using relations (7) and (8). We will illustrate this

with the example of monodeuterated ethylene. In the case of a single isotope substitution, relations (7) and (8) simplify to relation (12). By using calculated perturbed frequencies $\nu_4 = 999.4 \text{ cm}^{-1}$, $\nu_7 = 945.7 \text{ cm}^{-1}$ and $\nu_8 = 804.8 \text{ cm}^{-1}$ one finds the corresponding normal modes Ψ_4 , Ψ_7 and Ψ_8 . These normal modes can be normalized using relation (10). In the case of monodeuterated ethylenes, this relation reduces to

$$\langle \Psi | \mathbf{M} + \Delta \mathbf{M} | \Psi \rangle = \sum_i c_i^* c_i + \Delta m_\tau \sum_{i,j} c_i^* c_j \langle \Phi_i | \tau \rangle \langle \tau | \Phi_j \rangle.$$

where $\Psi = \sum_i c_i \Phi_i$. With the convention that x -axis points in the direction of the CC bond, normalized vibrations Ψ_4 , Ψ_7 and Ψ_8 thus obtained are:

$$\begin{aligned} \Psi_4 &= 0.01615\Phi_{T_z} + 0.04259\Phi_{R_x} + 0.02566\Phi_{R_y} - 0.85524\Phi_4 + 0.40313\Phi_7 + 0.30991\Phi_8 \\ \Psi_7 &= 0.00204\Phi_{T_z} + 0.00539\Phi_{R_x} + 0.00325\Phi_{R_y} - 0.03125\Phi_4 + 0.65185\Phi_7 + 0.75760\Phi_8 \\ \Psi_8 &= 0.08862\Phi_{T_z} + 0.23377\Phi_{R_x} + 0.14081\Phi_{R_y} - 0.37774\Phi_4 - 0.55284\Phi_7 + 0.50042\Phi_8 \end{aligned} \quad (17)$$

One can now verify that these vibrations satisfy the orthonormality relation (3'). This is an independent proof that the above LRP method is consistent and valid.

In the above example, we have considered six deuterated ethylenes. However, each ethylene hydrogen atom can be substituted either with a deuterium or with a tritium, in all possible combinations. There are 26 such isotopomers. To obtain out-of-plane frequencies and normal modes of all these isotopomers by the LRP method, no additional information (except for the mass of tritium atom) is required. To this list one can add various possible combinations with ^{12}C and ^{13}C isotopes. This increases the number of all possible isotopomers to 98. Out-of-plane frequencies and the corresponding normal modes of all these isotopomers can be obtained using only three ethylene out-of-plane frequencies. This relates a huge amount of experimental data to only three experimental quantities, ethylene out-of-plane frequencies ν_4 , ν_7 and ν_8 .

It should be noted that another type of connections between vibrational frequencies of isotopic molecules can be obtained by various isotopic rules. Such rules are the product rule⁶ the sum rule⁷ and the complete isotopic rule⁸. For example, the complete isotopic rule concerns three isotopic molecules (A, B and C). These molecules must be in special relations: molecule A is a plane molecule in which two definite atoms form a symmetrically equivalent set. B is identical to A except that one of these two atoms is exchanged for an isotope, and C is identical to A and B except that both of these two atoms are exchanged for this isotope.⁸ An example is the set of

three molecules: ethylene, ethylene-*d*1 and *trans*-ethylene-*d*2. From the known frequencies of compounds A and C, one can now calculate frequencies of compound B.

There are important differences between isotopic rules and the LRP method. All isotopic rules provide only information about frequencies, while the LRP approach determines also the corresponding normal modes. Further, as illustrated in the above ethylene case, the LRP method produces in a systematic way out-of-plane frequencies of all ethylene isotopomers using only ethylene out-of-plane frequencies. In order to apply the complete isotope rule, one has to know frequencies of the two isotope molecules A and C. These molecules differ in a very special way. Only in this way can one obtain frequencies of the third molecule B, which is intermediate between molecules A and C. Similar restrictions apply to other isotopic rules.

CONCLUSION

The LRP method was applied to the vibrational isotope effect. The out-of-plane vibrations of planar molecules were considered. Relations for these frequencies and the corresponding normal modes of the perturbed molecule are given. This LRP method is demonstrated on the example of deuterated ethylenes. All six deuterated ethylenes were considered. In order to obtain out-of-plane frequencies and the corresponding normal modes of these isotopomers, only three out-of-plane frequencies of the ethylene molecule are required.

Theoretical (LRP) out-of-plane frequencies are in excellent agreement with experimental out-of-plane frequencies for all deuterated ethylenes (Tables III and IV). The standard error for all frequencies is 2.92 cm^{-1} .

Due to the high symmetry of ethylene molecule, ethylene out-of-plane frequency ν_4 is inactive and hence its experimental value $\nu_4 = 1024\text{ cm}^{-1}$ is not very reliable. One can use out-of-plane frequencies of deuterated ethylene in order to improve out-of-plane frequencies of unsubstituted ethylene. One obtains that the choice $\nu_4 = 1028.2\text{ cm}^{-1}$, $\nu_7 = 950.1\text{ cm}^{-1}$, and $\nu_8 = 942.2\text{ cm}^{-1}$ minimizes standard error for out-of-plane frequencies of deuterated ethylenes (standard error decreases from $\Delta = 2.92\text{ cm}^{-1}$ to $\Delta = 2.35\text{ cm}^{-1}$). These optimum values only negligibly correct experimental frequencies ν_7 and ν_8 . However, frequency ν_4 , whose experimental value is relatively unreliable, changes much more substantially. This suggests that ethylene frequency ν_4 should be closer to the value of $\nu_4 = 1028.2\text{ cm}^{-1}$, which minimizes standard error, than to the value of $\nu_4 = 1024\text{ cm}^{-1}$.

Besides out-of-plane frequencies of polysubstituted isotopomers, the LRP approach provides also the corresponding normal modes. This is demonstrated by the derivation of the out-of-plane normal modes for molecule

C_2H_3D . Calculated normal modes are orthogonal to each other, as required by the hermiticity of the perturbed eigenvalue equation. Mutual orthogonality of perturbed normal modes demonstrates the consistency of the LRP approach.

The LRP approach is not restricted to the ethylene molecule, but it can be equally applied to all planar molecules and also to in-plane vibrations of planar molecules.⁵

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SAŽETAK

Vibracijski izotopni efekt planarnih molekula pomoću metode perturbacije niskog ranga: deuterirani etileni

Tomislav P. Živković

Razmatrane su planarne molekule A i B koje se razlikuju u izotopnim supstitucijama na atomima τ . Izvanravnijske frekvencije ω_k i normalni modovi Ψ_k perturbirane izotopne molekule B izražene su kao funkcije izvanravnijskih frekvencija ν_i i normalnih modova Φ_i neperturbirane molekule A. Potpuna specifikacija neperturbiranih normalnih modova Φ_i nije potrebna. Potrebne su samo amplitude $\langle \tau | \Phi_i \rangle$ normalnih modova Φ_i na mjestima τ izotopne supstitucije. Izvedeno je pravilo češlja koje učešljuje frekvencije ω_k s frekvencijama ν_i . Metoda je primijenjena na deuterirane etilene. Izvanravnijske frekvencije deuteriranih etilena zadovoljavaju pravilo češlja. Postoji samo jedno ozbiljno neslaganje, koje vjerojatno ukazuje na eksperimentalnu pogrešku. U slučaju etilena izvanravnijske amplitude $\langle \tau | \Phi_i \rangle$ određene su simetrijom molekule. Stoga izvanravnijske frekvencije i normalni modovi deuteriranih etilena ovise samo o eksperimentalnim izvanravnijskim frekvencijama etilena. Standardna pogreška izračunanih izvanravnijskih frekvencija deuteriranih etilena iznosi samo 2.92 cm^{-1} .